

PATENT SPECIFICATION

(11) 1 478 979

1 478 979

- (21) Application No. 52180/73 (22) Filed 9 Nov. 1973
 (23) Complete Specification filed 7 Nov. 1974
 (44) Complete Specification published 6 July 1977
 (51) INT CL² C23F 7/26
 (52) Index at acceptance
 C7U 4A 4C 4E3 4J 4P 7A 7C 7G
 C3P 102 8D3A 8D4 8K8 8K9 9D1A3 9K8 E2 PC14A
 PC20B PC7 PC8B PC8C
 (72) Inventor GARY EDMUND WILLIAMS



(54) IMPROVEMENTS IN THE CHROMATING OF METALS

(71) We, BRITISH STEEL CORPORATION, a Corporation incorporated and existing under the Iron & Steel Act 1967, of 33 Grosvenor Place, London, S.W.1, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the surface treatment of metals in order to increase corrosion resistance. The invention is particularly concerned with a chromate-resin composition for use as a paint primer on the surfaces of metals such as steel, zinc and aluminium.

It has been found that the conventional chromate-resin coating compositions presently used as paint primers for metal surfaces suffer from certain disadvantages. In the case where the chromate-resin composition is selected for its ability to protect the metal surface from corrosion, the adhesion of the paint to the metal surface is frequently found to be poor. On the other hand in the case where the chromate-resin composition is selected for its effectiveness for paint adhesion, it is found that its ability to protect the metal surface against corrosion is poor. It is therefore an object of the present invention to provide a chromate-resin composition which not only protects the metal against corrosion, but also enables paint to adhere to the metal surface effectively.

According to one aspect of the present invention a composition for the surface treatment of a metal comprises an aqueous solution containing chromium ions having a Cr^{VI} to Cr^{III} ratio lying between 2:1 and 3:2 together with a water soluble organic resin.

According to another aspect of the present invention a method for the surface treatment of a metal comprises applying to the surface of the metal an aqueous solution containing chromium ions having a Cr^{VI} to Cr^{III} ion ratio lying between 2:1 and 3:2 together with a water soluble organic resin and drying the solution to form a film.

The aqueous solution may contain the

chromium ions in any one of the following three forms although other forms are not excluded:—

- (a) A hexavalent chromium compound which has been partially reduced to the trivalent state,
- (b) A trivalent chromium compound which has been partially oxidized to the hexavalent state —
- (c) A mixture of hexavalent and trivalent chromium compounds.

The aqueous solution may be applied to the surface of the metal by any conventional method, for example by immersion, spray, squeegee or coil coater. The temperature at which the solution is applied may be from ambient to 60°C and preferably the solution is dried after application at any suitable temperature not exceeding 250°C. The chromium weight of the film produced on drying the solution conveniently lies within the range 0.03 to 0.20 g/m², while the total film weight lies within the range 0.1 to 0.5 g.

Suitably the solution contains the chromium ions in the form of a partially reduced hexavalent chromium compound.

Conveniently the organic resin is a copolymer of acrylonitrile, itaconic acid, a butylated urea and acrylamide. The resin may contain from 30 to 60% acrylonitrile by weight, from 30 to 60% itaconic acid by weight, from 5 to 30% of the butylated urea by weight and from 5 to 20% acrylamide by weight.

The solution may contain the partially reduced hexavalent chromium compound in an amount lying within the range 3 to 20 g/l, preferably within the range 5 to 10 g/l and the resin in an amount lying within the range 10 to 50 g/l preferably within the range 10 to 30 g/l. The solution may also contain hydro-fluorosilicic acid as a corrosion inhibitor in an amount for example lying within the range 2 to 5 g/l, although preferably within the range 2 to 3 g/l.

Sugar has been found to be effective as an agent for reducing the compound when present in the solution. A suitable sugar is dextrose.

Other compounds such as ammonium fluoride, 1,2-bipyridyl, 1,10-phenanthroline and fluoroboric acid — may also be incorporated in the solution to increase the corrosion resistance of the coated metal surface. The ammonium fluoride may be present in an amount within the range 0.5 to 2.0 g/l, the 1,2-bipyridyl and 1,10-phenanthroline in amounts lying with the range 0.25 to 1.0 g/l respectively and the fluoroboric acid in an amount lying within the range 1 and 5 g/l.

In the case where the metal surface is to be painted it has been found that the ratio of Cr^{VI} to Cr^{III} ions is of some importance in order to obtain good adhesion between the paint and the metal surface and to protect the painted surface from the effects of corrosion. A higher ratio than that defined above tends to produce deterioration of the corrosion resistance, while a lower, ratio tends to reduce the adhesion of the paint to the metal surface. The water soluble resin is also a useful constituent of the composition of the present invention since it aids paint adhesion and increases the corrosion resistance of the metal surface.

Embodiments of the invention will now be particularly described with reference to the examples hereinbelow:—

Example 1.

100 grams of chromic acid were dissolved in 1 litre of water and 5 grams D (+) - dextrose were added to the solution. The mixture was boiled for two hours to dissolve the dextrose which was effective to partially reduce the chromic acid to give a Cr^{VI} to Cr^{III} ion ratio of 3:2.

The above solution was used to make up a further solution having the following constituents:—

Solution A

Partially reduced chromic acid solution (with Cr^{VI} to Cr^{III} ion ratio of 3:2 and the concentration based on the initial chromic acid concentration)

6 g/l

Water soluble organic resin (Copolymers of itaconic acid 40%, acrylonitrile 40%, acrylamide 10% and butylated urea 10%)

10 g/l

Hydrofluorosilicic acid, R_2SiF_6

2.5 g/l

Ammonium fluoride, NH_4F

1 g/l

1,10-phenanthroline

0.5 g/l

Four cold reduced mild steel panels were cleaned and one was coated by spray coating with solution "A" at ambient temperature, another with a conventional chromate resin system, another with a conventional chromate silicate system while one was left untreated. The coated panels were then dried at 150°C and the four panels were placed in an atmosphere of condensing humidity for 168 hours after which the corrosion products were removed by Clark's solution (1 litre conc. hydrochloric acid, 14 g antimony trichloride and 10 g stannous chloride) and the weight loss noted.

Table 1 shows the weight loss noted in each case. It will be seen that the panel treated with solution "A" was far less corroded than the other panels.

TABLE 1

| Coating Solution | Wt. Loss in mg/sq.ft. |
|---------------------------------------|-----------------------|
| Untreated | 2130 |
| Solution "A" | 138 |
| Conventional chromate resin system | 210 |
| Conventional chromate silicate system | 173 |

Example 2.

Four cold reduced mild steel panels were selected and three were cleaned and coated as in Example 1 while one was left untreated after cleaning. The panels were then painted with an acrylic paint and were then tested for adhesion and corrosion inhibition in a

humidity cabinet, a salt spray and an SO_2 cabinet respectively.

In order to determine adhesion characteristics, a small sample of each panel was cross-hatched by means of a scribe and an Erichsen indentation of 9 mm was produced over the area of the cross hatch. Attempts were then

made to remove paint from the cross-hatch by means of adhesive tape. The results tabulated in Table II are the percentage of cross-hatched squares of paint removed.

5 The humidity test was conducted for 2000 hours, the salt spray test for 1000 hours and the SO₂ cabinet test after 20 cycles. The corrosion characteristics of each panel were determined by the visual inspection of a

scribed section of each panel. The results are also shown in Table II where the frequency and size of paint blisters are expressed according to the following scale:—

Frequency of blisters:

F, few; M, medium, D, dense,

Size of blisters:

8 very small; 6, medium size; 2, very large.

10

15

TABLE II

| Nature of Test | Untreated | Solution A | Chromate Resin System | Chromate Silicate System |
|-------------------------|---------------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Adhesion | 100% | 0% | 0% | 0% |
| Humidity | Dense rust in scribe. D8 blisters | Slight rust in scribe | Heavy rust in scribe | Heavy rust in scribe |
| Salt Spray | Dense rust in scribe. D6 blisters | Heavy rust in scribe | Heavy rust in scribe | Very heavy rust in scribe |
| SO ₂ Cabinet | Dense rust in scribe. D2 blisters. | Rust in scribe. D8 blisters | Rust in scribe. D6 blisters | Rust in scribe. D8 blisters |

20 It will be seen from Table II that the panel treated with solution "A" has excellent adhesion values, and that it was far less corroded than the other panels.

Example 3.

25 Panels of hot dip galvanised steel, electro-galvanised steel and hot dip aluminised steel were cleaned and coated with solution "A" by the procedure of Example 1 and three

further panels were cleaned and coated with conventional reduced chromate-resin system. The panels were then painted with an acrylic and an alkyd paint and tested as in Example 2. The results are shown in Table III using the same scale of blister size and frequency as above. The adhesion results refer to the Erichsen indentation produced over a cross-hatch before paint can be removed by means of adhesive tape.

30

35

TABLE III

| Substrate | Test Method | Solution 1 | | Conventional chromate resin | |
|--------------------------|-----------------|--------------------------------|----------------------------|-----------------------------|------------------------------------|
| | | Acrylic | Alkyd | Acrylic | Alkyd |
| Hot Galvanised steel | Adhesion | 7 mms | 8 mms | 6 mms | 6 mms |
| | Humidity | No change | No change | No change | F6 blisters near scribe |
| | Salt Spray | No change | No change | No change | No change |
| | SO ₂ | D8 blisters | D6 blisters | D8 blisters | D6 blisters |
| Electro Galvanised Steel | Adhesion | 8 mms | 8 mms | 6 mms | 7 mms |
| | Humidity | No change | No change | D8 blisters near scribe | D8 blisters near scribe |
| | Salt Spray | F6 blisters | M6 blisters | D4 blisters | D4 blisters |
| | SO ₂ | F6 blisters | F6 blisters | F6 blisters | F6 blisters |
| Hot dip Aluminised Steel | Adhesion | 9 mms | 9 mms | 9 mms | 9 mms |
| | Humidity | No change | No change | No change | No change |
| | Salt Spray | F6 blisters | F6 blisters | F8 blisters | F8 blisters |
| | SO ₂ | Red rust in scribe F8 blisters | Rust in scribe F8 blisters | Rust in scribe F8 blisters | Slight rust in scribe, F8 blisters |

It will be seen that the panels coated with solution "A" exhibited superior adhesion and corrosion properties as compared with the conventional chromate resin.

5 WHAT WE CLAIM IS:—

1. A composition for the surface treatment of a metal comprising an aqueous solution containing chromium ions having a Cr^{VI} to Cr^{III} ion ratio lying between 2:1 and 3:2 together with a water soluble organic resin.

10 2. A composition as claimed in claim 1 in which the aqueous solution contains the chromium ions in any one of the following forms:

15 (a) A hexavalent chromium compound which has been partially reduced to the trivalent state,

(b) A trivalent chromium compound which has been partially oxidised to the hexavalent state or,

20 (c) A mixture of hexavalent and trivalent chromium compounds.

3. A composition as claimed in claim 1 or claim 2 in which the organic resin is a copolymer of acrylonitrile, itaconic acid, a butylated urea and acrylamide.

4. A composition as claimed in claim 3 in which the resin contains from 30 to 60% acrylonitrile by weight, from 30 to 60% itaconic acid by weight, from 5 to 30% of the butylated urea by weight and from 5 to 20% acrylamide by weight.

5. A composition as claimed in any of claims 2 to 4 in which the solution contains the partially reduced hexavalent chromium compound in an amount lying within the range 3 to 20 g/l, preferably in an amount lying within the range 5 to 10 g/l.

6. A composition as claimed in any preceding claim in which the solution contains the resin in an amount lying within the range 10 to 50 g/l, preferably in an amount lying within the range 10 to 30 g/l.

7. A composition as claimed in any preceding claim in which the solution contains hydro-fluorosilicic acid as a corrosion inhibitor in an amount, for example, lying within the range 2 to 5 g/l, although preferably in an amount lying within the range 2 to 3 g/l.

8. A composition as claimed in any preceding claim in which sugar is present in the solution and is effective as a reducing agent.

9. A composition as claimed in claim 8 in which the sugar is dextrose.

10. A composition as claimed in any preceding claim in which the solution also contains any one or more of the following compounds which are effective to increase the corrosion resistance of the metal surface when coated:— ammonium fluoride, 1,2-bipyridyl, 1,10-phenanthroline and fluoroboric acid.

11. A composition as claimed in claim

2.0 g/l, the 1,2-bipyridyl and 1,10-phenanthroline in amounts lying within the range 0.25 to 1.0 g/l respectively and the fluoroboric acid in an amount lying within the range 1 to 5 g/l.

12. A method for the surface treatment of a metal comprising applying to the surface of the metal an aqueous solution containing chromium ions having a Cr^{VI} to Cr^{III} ion ratio lying between 2:1 and 3:2, together with a water soluble organic resin, and drying the solution to form a film.

13. A method as claimed in claim 12 in which the aqueous solution contains the chromium ions in any one of the following forms:—

(a) A hexavalent chromium compound which has been partially reduced to the trivalent state,

(b) A trivalent chromium compound which has been partially oxidised to the hexavalent state, or

(c) A mixture of hexavalent and trivalent chromium compounds.

14. A method as claimed in claim 12 or claim 13 in which the aqueous solution is applied to the surface of the metal by any conventional method, for example by immersion, spray, squeegee or coil coater.

15. A method as claimed in any of claims 12 to 14 in which the solution is applied at any temperature lying between ambient and 60°C.

16. A method as claimed in any of claims 12 to 15 in which the solution is dried after application at any suitable temperature not exceeding 250°C.

17. A method as claimed in any of claims 12 to 16 in which the chromium weight of the film produced on drying the solution lies within the range 0.03 to 0.20 g/m² while the total film weight lies within the range 0.1 to 0.5 g/m².

18. A method as claimed in any of claims 12 to 17 in which the organic resin is a copolymer of acrylonitrile, itaconic acid, a butylated urea and acrylamide.

19. A method as claimed in claim 18 in which the resin contains from 30 to 60% acrylonitrile by weight, from 30 to 60% itaconic acid by weight, from 5 to 30% of the butylated urea by weight and from 5 to 20% acrylamide by weight.

20. A method as claimed in any of claims 13 to 19 in which the solution contains the partially reduced hexavalent chromium compound in an amount lying within the range 3 to 20 g/l, preferably in an amount lying within the range 5 to 10 g/l.

21. A method as claimed in any of claims 12 to 20 in which the solution contains the resin in an amount lying within the range 10 to 50 g/l, preferably within the range 10

- 12 to 21 in which the solution also contains hydro-fluorosilicic acid as a corrosion inhibitor in an amount lying within the range 2 to 5 g/l, preferably in an amount lying within the range 2 to 3 g/l. 5
23. A method as claimed in any of claims 12 to 22 in which sugar is present in the solution and is effective as a reducing agent.
24. A method as claimed in claim 23 in which the sugar is dextrose. 10
25. A method as claimed in any of claims 12 to 24 in which the solution contains any one or more of the following compounds which are effective to increase the corrosion resistance of the metal surface when coated:— ammonium fluoride, 1,2-bipyridyl, 1,10-phenanthroline and fluoroboric acid. 15
26. A method as claimed in claim 25 in which the ammonium fluoride is present in an amount lying within the range 0.5 to 2.0 g/l, the 1,2-bipyridyl and 1,10 phenanthroline in amounts lying within the range 0.25 to 1.0 g/l respectively and the fluoroboric acid in an amount lying within the range 1 to 5 g/l. 25
27. A composition as claimed in any of claims 1 to 11 with reference to any of the examples.
28. A method as claimed in any of claims 12 to 26 substantially as hereinbefore described with reference to any of the examples. 30
29. A metal substrate whenever treated with the composition as claimed in any of claims 1 to 11 and 27.
30. A metal substrate treated by the method as claimed in any of claims 12 to 26 and 28. 35

G. RENTON,
Agent for the Applicants.